J. Japan. Assoc. Min.
Petr. Econ. Geol.,
71, 183~192, 1976

A NEW COPPER SULFATE–CARBONATE HYDROXIDE HYDRATE MINERAL, $(Mn, Ni, Cu)_8(SO_4)_4(CO_3)(OH)_6 \cdot 48H_2O$, FROM NAKAURI, AICHI PREFECTURE, JAPAN

JUJIN SUZUKI

Department of Earth Sciences, Aichi University of Education, Kariya

MASAHIRO ITO

Laboratory of Earth Sciences, Department of General Education, Nagoya University, Nagoya

TSUTOMU SUGIURA

Department of Chemistry, Aichi University of Education, Kariya

Nakauriite is a new mineral found as fissure-fillings in serpentinite. There are two types appearing in different modes of occurrences, and showing a few faint differences in X-ray diffraction and DTA patterns. Both show very fine needle-like and prismatic forms with characteristic sky-blue color. It is effervescent in HCl, H_2SO_4 and HNO_3. Chemical analysis gave $Mn_{0.019}Ni_{0.231}Cu_{7.770}(SO_4)_{3.904}(CO_3)(OH)_{6.232}48.4H_2O$ or $(Mn, Ni, Cu)_8(SO_4)_4(CO_3)(OH)_6 \cdot 48H_2O$ as C=1 for empirical cell contents. The most intense X-ray diffraction lines (in Å) are 7.31 (100), 4.840 (14), 3.936 (14), 3.652 (20), 3.552 (13), 2.397 (14), 2.367 (16), 2.332 (14) and 1.9148 (16). The 7.823Å-line appears with variable intensities. Nakauriite is pleochroic, X=colorless, Y=very light greenish blue, Z=pale sky-blue to very light blue. The mineral is biaxial negative with $\alpha=1.585$, $\beta=1.604$, $\gamma=1.612$ (all±0.001), 2V(-)=65.3 (calc.), showing positive elongation. Extinction is parallel to the outline. Five endothermic reactions are found at 78, 150, 186, 330 and 396°C of peak maxima, respectively, the last two being characteristically strong. Infrared absorption gives two characteristic bands at 3000 and 1360 cm^{-1}. The name is for the locality.

INTRODUCTION

At first, this very clear sky-blue mineral was found on some serpentinite fragments removed from an abandoned mine in Sambagawa metamorphic belt at Nakauri, about 6 km southeast of Shinshiro, Aichi Prefecture, Japan. Soon after, this mineral was noted to occur as fracture-fillings in the brucite-bearing serpentinite mass and was named nakauriite for the locality. The mineral and the name were approved in advance of publication by the Commission on New Minerals and Mineral Names, IMA.

Many species of ore minerals have been known in the serpentinite mass, that is, magnetite, native copper, chalcocite, cuprite, digenite, djurleite, cobalt pentlandite, heazlewoodite, and as secondary minerals, tenorite, malachite, brochantite and azurite.

Only two sulfate-carbonate hydroxide hydrate minerals have been reported so far: carbonate-cyanotrichite (Ankinovich *et al.*, 1963) and jouravskite (Graudefroy and Permingeat, 1965). Nakauriite is the third

---

(Manuscript recieved, April, 2, 1976)

one of this kind. In this paper, detailed description of this mineral will be reported in comparison with that of carbonate-cyanotrichite which is somewhat similar to nakauriite in appearance.

MODE OF OCCURRENCE

Nakauriite which is conspicuously sky-blue in color by the naked-eye is found as fissure-fillings in the fractured serpentinite body containing hard and massive serpentinite blocks. The serpentinite is composed mainly of serpentine minerals, opaque minerals, brucite, pyroaurite, artinite, hydromagnesite, "yoshikawaite"[1] (Suzuki and Ito, 1973), coalingite and aragonite. Coalingite occurs as veins associated with pyroaurite.

Nakauriite shows two modes of occurrences: Type 1 and Type 2.

Type 1 occurs as veins cutting the massive serpentinite and the fractured serpentinite. The mineral is commonly associated with chrysotile and a small amount of magnetite, and rarely with brochantite and malachite in massive serpentinite. Type 2 occurs along fractures in sheared serpentinite. It is commonly associated with chrysotile, magnetite, artinite and pyroaurite. Free growth of very fine-grained slender crystal aggregates of the mineral is commonly found in the small openings of fractured serpentinite (Fig. 1.). Crystals of Type 2 are relatively smaller than those of Type 1, commonly associated with fair amounts of extremely fibrous ones.

Any distinguishable differences in chemical composition and optical properties are not observed between the two types. However, some slight differences are noticed in X-ray diffraction and DTA patterns, which will be discussed in each section mentioned below.

Fig. 1. A mode of occurrence of nakauriite.

OPTICAL AND OTHER PHYSICAL PROPERTIES

Nakauriite occurs commonly as bundled aggregates of very small slender to fibrous crystals, whose sizes are less than about 0.2 mm in length, 0.006 mm in width. It is clear sky-blue in color and pleochroic with X=colorless, Y=very light greenish blue, Z=pale sky-blue to very light blue. The refractive indices for sodium light are $\alpha=1.585\pm0.001$, $\beta=1.604\pm0.001$, $\gamma=1.612\pm0.001$ by the immersion method. Birefringence is moderate; $\gamma-\alpha=0.027$, $\beta-\alpha=0.019$, $\gamma-\beta=0.009$. The mineral is biaxial negative with 2V(-) 65.3° (calculated). Extinction is parallel to the outline of the crystal with positive elongation. Cleavage and twinning are not observed.

The density was determined by flotation of clear crystals in Clerici solution, which gave a value of 2.39±0.02 g/cm^3. The density calculated by Gradstone and Dale's equation is 2.30 g/cm^3, in well agreement with the observed value.

---

1) Application to the IMA Commission on New Minerals and Mineral Names for an approval of the name is pending.

Carbonate-cyanotrichite shows similar pleochroism, but has higher refractive indices and double refraction, showing optically positive sign and negative elongation.

CHEMICAL COMPOSITION

The sample which was thoroughly purified was used for qualitative analysis by X-ray fluorescence method. Electron probe microanalysis was also made in order to check the validity of the data obtained by the X-ray fluorescence analysis. As the specimen is too brittle to prepare evenly polished section for EPMA, hand-picked specimen mounted on extremely pure beryllium plate was carbon-coated as it was. Effervescency in HCl, H_2SO_4 and HNO_3 positively shows the presence of CO_3-component in nakauriite. Although the sample was prepared by careful hand-picking under the binocular microscope, even the most purified concentrate was still found to be contaminated by chrysotile, judged from the data of DTA.

Table 1. Chemical compositions of nakauriite and associated chrysotile from Nakauri, Achi Prefecture, Japan.

	A	B	C
SiO_2	28.56	42.56	0
TiO_2	0.02	0.03	0
Al_2O_3	0.09	0.16	0
Fe_2O_3	0.19	0.26	0.06
MgO	28.50	42.51	0
MnO	0.08	0.08	0.09
CaO	0.02	0.03	0
Na_2O	0.01	0.02	0
K_2O	0.01	0.02	0
CuO	10.57	-	32.12
NiO	0.35	0.09	0.88
ZnO	0.02	0.02	0.03
$H_2O(+)$	24.11	13.72	45.31
$H_2O(-)$	1.35	0.54	3.01
SO_3	5.34	-	16.23
CO_2	0.75	-	2.28
Total	99.97	100.04	100.01

A. Nakauriite and the admixed chrysotile.
B. Chrysotile associated with nakauriite.
C. Nakauriite, corrected for the admixed chrysotile and normalized.

Quantitative chemical analysis for the purified sample was made by atomic absorption analysis for CaO, MgO, total iron, MnO and CuO, flame spectrochemical analysis for Na_2O and K_2O, titration method for Fe_2O_3,

Table 2. X-ray powder diffraction data for nakauriite from Nakauri, Aichi Prefecture, Japan.

Type 1			Type 2	
d	I/I₀	hkl 1)	d	I/I₀
7.819	<1	111	7.823	12
7.314*	100	200	7.308*	100
7.081**	14**	102	7.115	4
5.114	3	121	4.827	12
4.840	14	300	4.464	5
4.666	1	301	3.929	14
4.468	4	310,122	3.654*	26
3.936	14	222,023, 312	3.551	9
3.652*	20	400	3.300	5
3.552	13	401	2.700	1
3.301	8	024	2.613	3
2.694	2	006,305	2.507	3
2.611	8	431	2.440*	2
2.538	1	242	2.397	9
2.437*	2	026	2.365	10
2.397	14	243	2.334	3
2.367	16	504	2.260	2
2.332	14	602	2.228	2
2.260	2	017	2.156	2
2.232	2	532	1.964	3
2.074	1	350	1.9137	10
1.9653	4	345	1.824	2
1.9148	16	713	1.723	2
1.859	2	155	1.663	2
1.825	3	800	1.642	3
1.7202	3	626	1.595	<1
1.6648	2	391	1.571	<1
1.6437	4	356	1.548	2
1.596	2	911	1.536	5
1.572	2	073	1.516	2
1.5500	4	429	1.4580	6
1.5395	4	840	1.400	1
1.515	1	752	1.2872	2
1.4580	7	10,0,0	1.2137	2
1.402	1	5,1,10		
1.352	1			
1.302	1			
1.2889	2			
1.2154	2			
1.2053	2			
1.1942	1			
1.1173	1			

* Plus serpentine mineral.
** For not-pulverized slender crystals.
1) Calculated by A. Kato. Orthorhombic, a 14.585, b 11.47, c 16.22Å, Z=2, density (calc) 2.35g/cm³.

gravimetric analysis for Al_2O_3, SiO_2 and H_2O, spectrophotometric analysis for TiO_2 and SO_4^{2-}, and volumetric analysis for CO_2. The chemical composition of the purified sample and the chrysotile associated with nakauriite are listed in Table 1, together with the rationalized mole percentages. Contamination effect by the admixed chrysotile was eliminated based on the SiO_2 content of the purified sample.

The formula of nakauriite is $Mn_{0.019}Ni_{0.231}Cu_{7.770}(SO_4)_{3.904}(CO_3)(OH)_{6.232}\cdot 48.4H_2O$, and is idealized as $(Mn, Ni, Cu)_8\ (SO_4)_4\ (CO_3)(OH)_6\cdot 48H_2O$ as C=1 for empirical cell contents. Although a very small amount of ZnO and Fe_2O_3 are found in the chemical analysis, these may be neglected for the chemical formula of the mineral. The mole ratio of SO_4 to CO_3 of nakauriite, carbonate-cyanotrichite and jouravskite is 4:1, 1:2 and 1:1, respectively.

X-RAY DATA

X-ray powder data for the new mineral were obtained, using Ni-filtered CuK_α radiation. The whole X-ray diffraction data at room temperature are shown in Table 2 and Figure 2. Nakauriite gives clearly different pattern from that for carbonate-cyanotrichite.

Some differences are noted in the X-ray diffraction patterns of Type 1 and Type 2 of nakauriite as follows: (1) The reflection line of 7.82 Å appears characteristically in Type 2, and shows change of peak height depending on the orientations; if the powder specimen is rubbed strongly on the holder, the peak height increases. Type 1 shows fairly faint reflection line of 7.82 Å,

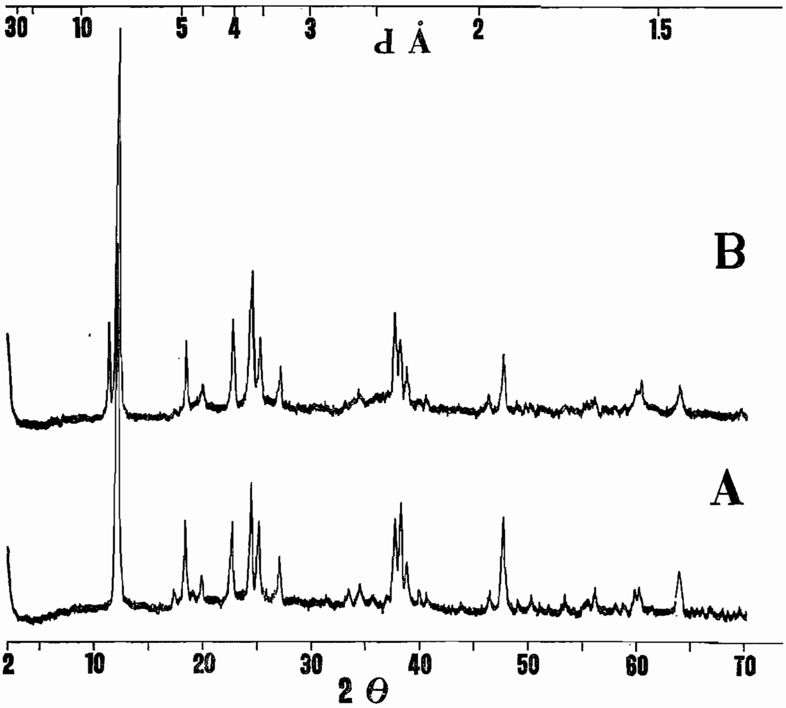

Fig. 2. X-ray diffraction patterns for nakauriite, A, Type 1; B, Type 2. CuK_α radiation was used for 2θ.

even undetectable in some cases. But it appears distinguishable when the sample is rubbed strongly on the holder.

(2) The patterns for the reflection lines of medium peak heights are characteristically different between the two types especially in the range of d-spacing of 5.54 to 3.43 Å and 2.43 to 2.31Å. Apparent peak heights of lines of 3.55 and 1.914Å are also distinctly different on the patterns between the two types. These relations in peak heights are not changed by orientation effect mentioned above.

(3) The whole reflection lines for Type 2 are generally weaker than those for Type 1.

The reflection lines of 7.31 and 3.65 Å may be assigned to those of the admixed chrysotile. But these lines are concluded to be essential ones for nakauriite, based on their thermal behaviours. The thermal effects on the whole X-ray diffraction patterns of the mineral were investigated by

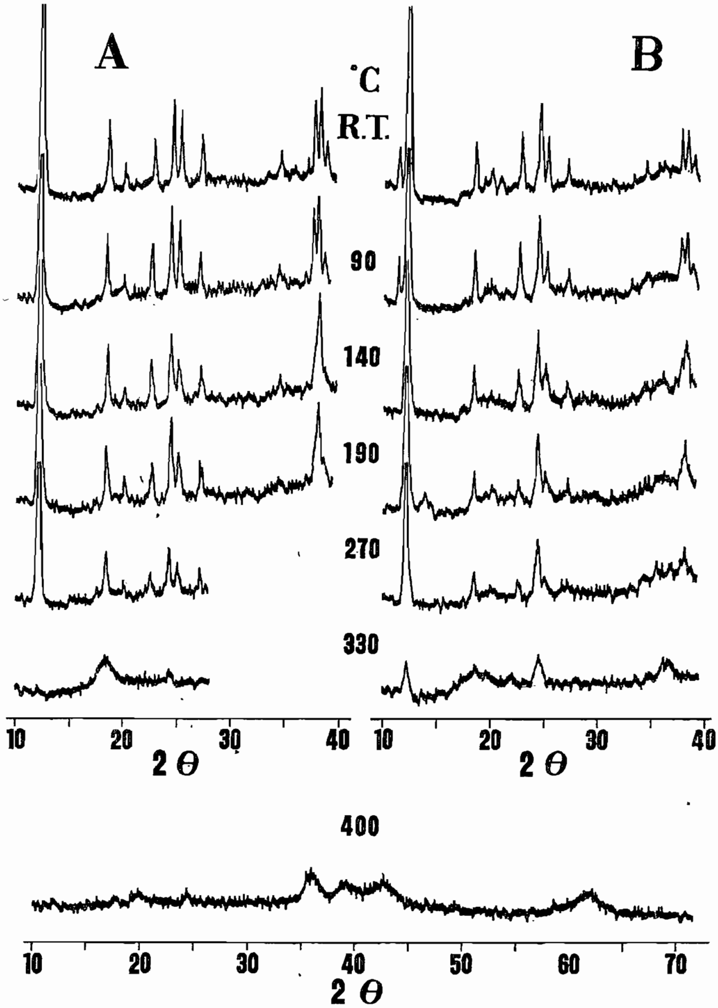

Fig. 3. X-ray diffraction patterns for thermal decomposition products of nakauriite at various temperatures. A, Type 1; B, Type 2. CuK_α radiation was used for 2θ.

the high temperature X-ray diffraction apparatus. The samples were heated in air up to various temperatures at the rate of 20°C per minute and held at the temperatures through X-ray diffraction measurements. Outline of the thermal effects is shown in Figure 3. The thermal behaviour above 250°C is practically the same between the two types. The reflection lines of 2.40 and 2.61 Å of Type 1 begin to be broadened at 180 and 190°C, respectively. Other lines decrease gradually the peak heights with rising temperature. At 400°C a decomposition phase is already formed showing some broad lines of 4.82, 3.66, 2.53, 2.29, 2.12 and 1.498 Å. The pattern obtained at 1000°C is neither tenorite nor cuprite. Such thermal changes of Type 1 just mentioned above are observed at comparatively higher temperatures than those of Type 2.

Thermal behaviour below 300°C of Type 2 of nakauriite is to be noted. The 7.82Å-line begins to decrease gradually its peak height and d-spacing with rising temperature above 90°C, and is hidden by the strong 7.31Å-line at 140°C. Broadening of 2.40 and 2.61 Å lines begins already at 90 and 140°C, respectively. A new broad line of 6.3 Å appears at 200°C, decreasing its d-spacing gradually with rising temperature to 6.03 Å at 280°C. At 400°C a perfectly new diffraction pattern for a decomposed phase appears, which is the same as that of Type 1.

The 7.8 Å-line reappears when the specimen heated below 240°C is cooled down to the room temperature, whose peak height is a half of the unheated one. This is probably due to the adsorption of water and possibly CO_2 in air.

THERMAL DATA

Simultaneous DTA-TG curves of nakauriite are shown in Figure 4. The heating rate is 20°C per minute. Two strong endotherms with maxima at 330 and 396°C are found, together with the three weak ones at 78, 150 and 186°C. The latter three endotherms are distinctly found for Type 2, but for Type 1 they are very faint.

The weight loss up to 240°C is estimated to be 2.8% (mean) for Type 1 and 3.3% (mean) for Type 2, on the TG curves, followed by correction for the admixed chrysotile and for the apparent mass-gain due to furnace air turbulence. The DTA patterns in the higher temperature region are

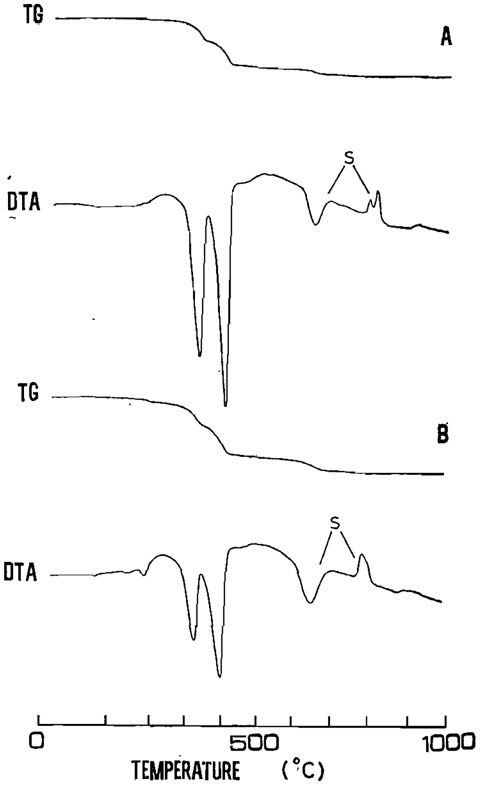

Fig. 4. Simultaneous DTA-TG patterns of nakauriite in air at atmospheric pressure. A, Type 1; B, Type 2. S=Admixed chrysotile. Heating rate is 20°C/min.

characteristically simple, showing only two strong endotherms, in contrast to that carbonate-cyanotrichite and jouravskite show fairly complex patterns. It should be stressed that such a simple pattern of nakauriite may suggest some informations on the bonding states of gaseous components in the crystal structure.

ELECTRON MICROSCOPIC DATA

Long prismatic morphology of nakauriite is clearly seen by the scanning electron microscopic photograph as shown in Figure 5a. The electron diffraction pattern is shown in Figure 5b, suggesting an orthorhombic lattice, which may be caused by heat effect due to electron beam. Figure 5c and 5d show electron microphotographs of the mineral with admixed serpentine mineral and the diffraction pattern of the latter mineral, respectively. Nakauriite is found as short lath-like crystals and the admixed serpentine mineral very long fiber and platy

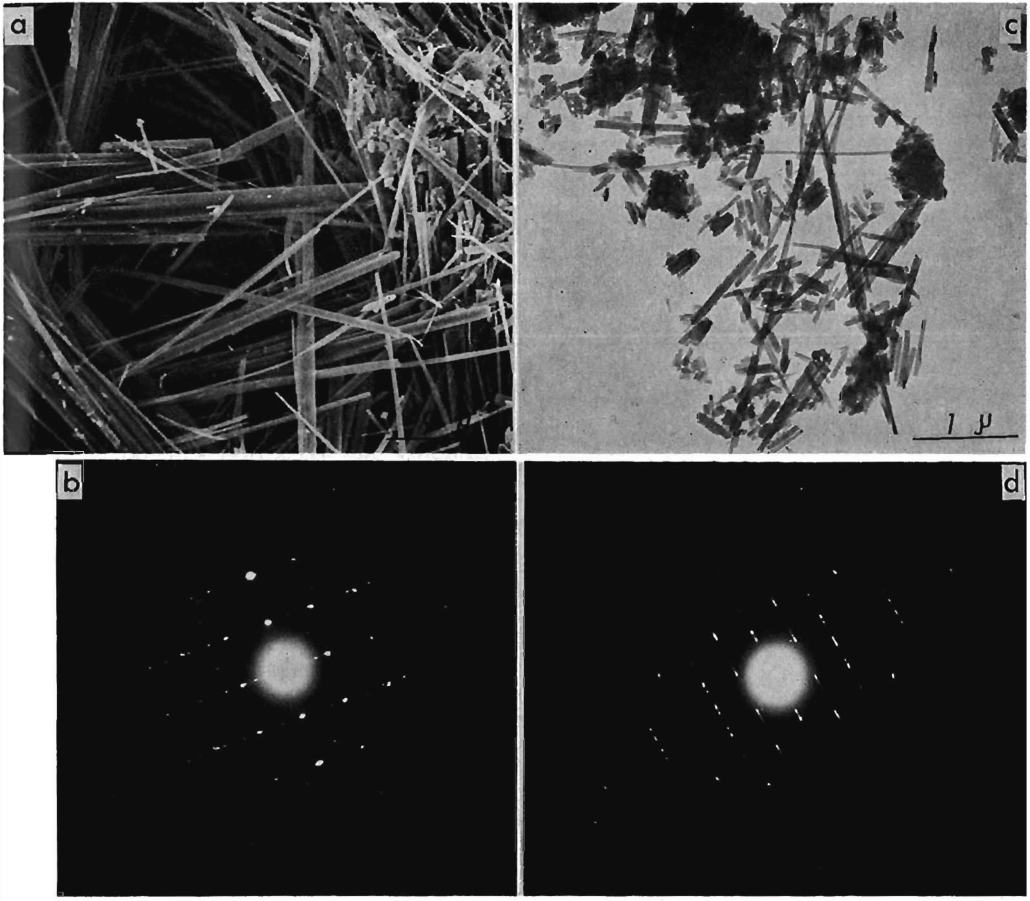

Fig. 5 a. Scanning electron microphotograph of nakauriite.
5 b. Electron diffraction pattern of nakauriite. Heat effect due to electron beam may be considered.
5 c. Electron microphotograph of nakauriite with admixed serpentine mineral.
5 d. Electron diffraction fiber photograph of chrysotile found in Figure 5c.

crystals. The diffraction photograph of the very long fibrous serpentine mineral shows the flared spots characteristically found in the diffraction pattern of chrysotile. The platy one is probably lizardite, a small amount of which is detected in the X-ray powder pattern.

INFRARED SPECTRA

Infrared absorption spectra of nakauriite and the associated serpentine mineral were obtained by the KBr disc technique as shown in Figure 6. The frequencies of bands are also shown in Table 3.

Some absorption bands are probably caused by the admixed serpentine mineral, as even the very carefully separated specimens of nakauriite always contain fair amounts of serpentine mineral. In 2000 to 4000 cm^{-1} region, two sharp and very strong bands are considered to be from the mineral and the admixed serpentine mineral, and the band around 3000 cm^{-1} is assigned to the mineral. Some differences in intensity of the absorption bands between the two types in this region may be explained by the amounts of admixed serpentine mineral. In 800 to 2000 cm^{-1} region, a broad and strong band of 1360 to 1355 cm^{-1} associated with a shoulder of 1405 cm^{-1} is characteristically observed, and assigned to the mineral. A few bands in 900 to 1100 cm^{-1} region may be assigned to the admixed serpentine mineral. In 400 to 800 cm^{-1} region, two strong bands are

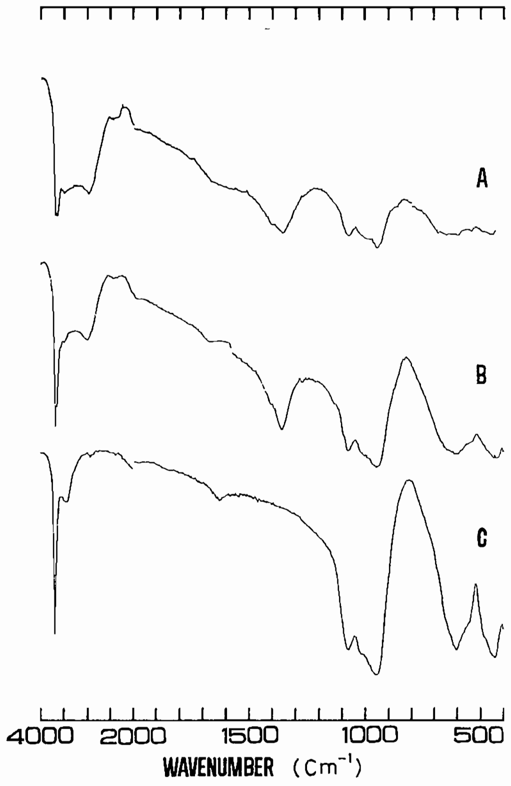

Fig. 6. Infrared absorption spectra of nakauriite and associated serpentine mineral. A, Type 1; B, Type 2 (all contain some amounts of serpentine mineral); C, serpentine mineral.

Table 3. Infrared absorption data (in cm^{-1}) for nakauriite and associated serpentine mineral from Nakauri, Aichi Prefecture, Japan.

A		B		C	
3700	s,sp	3700	s,sp	3699	s,sp
3650	s,sp	3652	s,sp	3655	m,sp
3500	m, b	3500	m, b	3450	m, b
2990	m, b	3000	m, b	2400	vw, b
2430	vw, b	2430	vw, b	1627	w, b
1660	sh	1640	plat	1075	s, b
1404	plat	1405	sh	1017	plat
1355	s, b	1360	s, b	950	s, b
1075	s, b	1078	s, b	604	s, b
1020	sh	1018	sh	489	sh
983	sh	990	sh	437	s, b
950	s, b	951	s, b		
613	s,vb	610	s, b		
454	s,vb	435	s, b		

A. Nakauriite (Type 1) with the admixed serpentine mineral.
B. Nakauriite (Type 2) with the admixed serpentine mineral.
C. Associated serpentine mineral.
s, strong; m, medium; w, weak; vw, very weak; sp, sharp; b, broad; vb, very broad; sh, shoulder; plat, plateau.

found in the pattern, which may be also caused by the admixed one.

It is important to note that any distinct differences are not found between the spectra of the two types of nakauriite.

DISCUSSIONS

Some differences are found in X-ray diffraction and DTA patterns of the two types of nakauriite, which are classified from the modes of occurrences.

The reflection lines of 7.82, 3.93, 2.61 Å and so on observed in the X-ray diffraction pattern of Type 2 may be assigned to those of pyroaurite commonly occurring in serpentinite. Judging from the peak heights relation of pyroaurite, most of these lines will overlap the pattern of Type 1. Thermal behaviour of pyroaurite was also investigated in order to solve this problem. Thermal change of pyroaurite begins clearly at lower temperature by 30°C than that of Type 2. Pyroaurite decreases the spacing of 7.82 Å to 7.75 Å at 80°C and to 7.61 Å at 120°C. By 140°C, this line is overlapped on 7.31 Å-line of the admixed serpentine mineral. During the thermal change of this line, a new broad reflection line of 6.46 Å appears distinctly, decreasing its d-spacing of 6.2 Å at 270°C. The 7.8 Å-line of pyroaurite is also rapidly revived from the 270°C heated sample after about only ten minutes of cooling at room temperature. Judging from these facts, it may be concluded that the thermal behaviour of Type 2 of nakauriite up to 300°C is similar to but is not identical with that of pyroaruite, and that the 7.8 Å-line of nakauriite is not caused by the admixed pyroaurite but is essential for nakauriite.

If so, why are some differences observed in the X-ray diffraction and the DTA patterns of the two types of the mineral ? Two interpretations may be possible.

1) The two types of the mineral are essentially not different. The observed slight differences are due to a small amount of water not affecting the crystal structure. A few reasons to support this explanation are as follows: (a) The 7.82 Å-line is also essential for Type 1, because this appears in Type 1 when the sample is well oriented in the holder. (b) The difference on the DTA patterns below 300°C between the two types is not essential, because Type 1 also shows the same though faintly, endotherms.

2) There are originally two types of nakauriite. The differences observed on the X-ray diffraction and DTA patterns between the two types are due to the different degree of mixing of the two. Some samples separeted as Type 2 may be admixed by various amounts of Type 1. Judging from the X-ray diffraction pattern, Type 1 will be comparatively less admixed with Type 2. However, it is impossible to discriminate strictly between these two types even under microscope, though Type 2 of nakauriite occurs in more fibrous form than Type 1.

In any case, it is very important to note that some n-order reflection lines of 7.82 Å are distinctly found on the diffraction pattern of Type 1, too, and that the infrared patterns are practically the same in respect to each other. Judging from these facts, the crystal structures of the two types are conjectured to be actually the same. Some features characteristically observed for Type 2 might be caused by the electron microscopically fibrous form and possibly small amount of loosely bounded water not affecting the crystal structure.

ACKNOWLEDGMENTS

Sincere thanks are due to Dr. K. Sakurai and Dr. A. Kato of National Science Museum, Prof. M. Nambu of Tohoku University, and Dr. Y. Tsuzuki of Nagoya University for much helpful suggestions and discussions. We are also indebted to Dr. I. Nishida of Nagoya University for kindly providing some of electron microphotographs and Dr. H. Nakata of Aichi University of Education and Mr. Y. Yusa of Nagoya University for kindly assisting in infrared spectra analysis and microprobe analysis, respectively.

REFERENCES

Ankinovich, E.A., Gekht, I.I. and Zaitseva, R. I. (1963), A new variety of cyanotrichite–carbonate-cyanotrichite. *Zapiski Vses. Mineralog. Obshch.*, **92**, 458–463. (in Russian)

Graudefroy, C. and Permingeat, F. (1965), La jouravskite, une nouvelle espèce minérale. *Bull. Soc. franç. Minér. Crist.*, **88**, 254–262.

Suzuki, J. and Ito, M. (1973), A new magnesium carbonate hydrate mineral, $Mg_5(CO_3)_4(OH)_2 \cdot 8H_2O$, from Yoshikawa, Aichi Prefecture, Japan. Jour. *Japan. Assoc. Min. Pet. Econ. Geol.*, **68**, 353–361.

愛知県中宇利産含 Ni, $Cu\text{-}SO_4\text{-}CO_3\text{-}OH\text{-}H_2O$ 鉱物の一つ，中宇利石について

鈴木　重人，伊藤　正裕，杉浦　孜

本鉱物は，三波川帯中の各種銅鉱物をともなう蛇紋岩体の割れ目より発見された。細かな針状ないし長柱状をなし，特徴的な sky-blue の色を呈する。構造式（C=1）として，

$$Mn_{0.019}Ni_{0.231}Cu_{7.770}(SO_4)_{3.904}(CO_3)(OH)_{6.232} \cdot 48.4H_2O$$

または，

$$(Mn, Ni, Cu)_8(SO_4)_4(CO_3)(OH)_6 \cdot 48H_2O$$ をもつ。

本鉱物の光学的性質，X 線回折，電子線回折，DTA-TG，IR パターンに見られる諸性質について報告した。また，産状の違いにより，X 線回折および DTA パターンに僅かな違いが見られ，これらについても検討した。

Nakauri, Shinshiro, Aichi Prefecture 愛知県新城市中宇利